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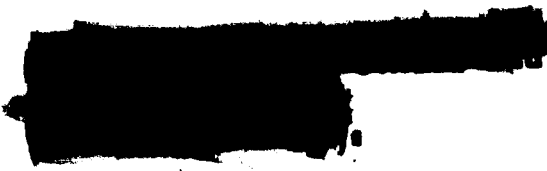
SOME CRITICAL MATERIALS PROBLEMS OF THERMIONIC
CATHODE SYSTEMS FOR FISSION-HEAT CONVERSION^{*}

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L. Yang, R. G. Hudson, F. D. Carpenter,
A. F. Weinberg, and S. Langer

This paper is being presented at the Symposium on Thermionic Power Conversion at Colorado Springs, Colorado, May 14-16, 1962, and will be published in the Proceedings of the Symposium.

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Abstract

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Two types of thermionic emitters have been suggested for the direct conversion of fission heat to electrical energy: (1) uranium-bearing carbides which also function as the nuclear fuels, and (2) refractory metals fueled with uranium containing oxides or carbides. Irrespective of what happens in a reactor, there are certain conditions which have to be met before these emitter systems can be of any practical value. For the carbide emitters, the rate of material loss by vaporization should satisfy the designed life expectancy at temperatures where useful performance is obtainable. For the refractory-metal emitters, the diffusion of the components of the fuels into the metals should not impair their electron-emission characteristics. The purpose of this paper is to analyze these aspects on the basis of existing experimental data and to discuss the current status and problem areas with regard to the feasibility of these two emitter systems.

Introduction

During recent years, considerable attention has been paid to two types of thermionic-cathode systems for the direct conversion of fission heat to electrical energy. These are the carbide-cathode system and the metal-cathode system. The former employs a uranium-containing carbide for the electron emitter as well as the fission-heat source, and the latter is composed of a refractory-metal electron emitter surrounding a uranium-containing nuclear fuel. In addition to in-pile materials problems due to the presence of radiation and fission products, certain out-pile materials problems are characteristic of each of these cathode systems. Unless solved, these out-pile problems will make it very difficult to select the proper conditions for in-pile studies of the systems. The purpose of this paper is to analyze some of these problems in the light of the experimental data available.

Carbide-cathode System

The carbide-cathode system operates at temperatures above 2000°K . Among all the uranium-containing carbides, the UC-ZrC solid solutions have received the most attention as materials for the carbide-cathode system. The various materials problems associated with this system have been discussed in two previous papers written at this Laboratory. [1, 2] The most critical problem is the loss of cathode materials by vaporization at temperatures where useful electron emission can be obtained. To select the operating temperatures for given life and performance requirements,

it is necessary to know the vaporization and electron-emission characteristics of the cathode materials. The present understanding of these properties for the UC-ZrC system is summarized below.

Vaporization Characteristics

The vaporization characteristics of the cathode materials in a thermionic cell are determined jointly by the thermodynamic stability and the diffusion properties of the materials. These involve the rate of vaporization, the uranium concentration near the surface region, and the variation in these quantities with time of heating. For the UC-ZrC system, it has been found that the vaporization characteristics depend strongly on whether or not the materials lost from the surface by vaporization are replenished by diffusion from the bulk. If the latter keeps pace with the former, then neither the rate of vaporization nor the uranium concentration near the surface region varies appreciably with time of heating. This is the case with the low-UC cathodes (14 to 20 mol-% UC) in the temperature range from 2100° to 2400° K and the high-UC cathodes (85 to 90 mol-% UC) at low temperatures (less than 2070° K). The rates of vaporization for these cathode materials lie in the range from 10^{-9} to 6×10^{-8} g/cm²/sec. In the temperature ranges indicated, the uranium depletion near the surface amounts to less than a few per cent for the low-UC cathodes and less than 10% for the high-UC cathodes.

On the other hand, if the rate of vaporization is much higher than the rate of diffusion, then both the rate of vaporization and the uranium concentration near the surface region decrease with time of heating. However, a plateau region is eventually reached where both these quantities vary only slightly with further heating. The vaporization characteristics of the high-UC cathodes (~90 mol-% UC) at high temperatures (e. g., 2300° K) fall into this category. For these materials, the rate of vaporization is initially very high ($\sim 10^{-6}$ g/cm²/sec) but drops to about 2×10^{-7} g/cm²/sec after 70 hr at 2300° K. At the same time, the uranium concentration near the surface region decreases to about one-third of the original value.

The observed rates of vaporization for the UC-ZrC system are summarized in Fig. 1.^[3]

Electron-emission Characteristics

The known vacuum electron-emission data for the UC-ZrC cathodes^[4-9] are plotted in Fig. 2. Included in the figure for the purpose of comparison are short-circuit currents obtained in some cesium cells with UC-ZrC cathodes.^[5, 8, 10-12] These data can be summarized as follows:

1. Results are more reproducible for the high-UC cathodes (~ 90 mol-% UC) than for the low-UC cathodes (~ 10 to 20 mol-% UC). By using a pulsed high-voltage supply, it has been possible to extend measurements on 90 mol-% UC-10 mol-% ZrC to temperatures of thermionic interest.^[4] Preliminary data indicate that an emission of 5 amps/cm² can be achieved at 2000°K.

2. For the low-UC cathodes (~ 10 to 20 mol-% UC), the results are still very confusing. The best data obtained in this Laboratory^[8] on 10 mol-% UC-90 mol-% ZrC (vacuum of $\sim 10^{-6}$ mm Hg) fall close to the earlier Los Alamos data^[6] on 20 mol-% UC-80 mol-% ZrC at temperatures below 1750°K, but are about a factor of seven higher than the average data^[8] obtained for 10 mol-% UC-90 mol-% ZrC in the same degree of vacuum. Unfortunately, these measurements do not extend to temperatures higher than 1900°K. Anderson and Danforth^[9] have studied the emission of 10 mol-% UC-90 mol-% ZrC between 1250°K and 2227°K, the vacuum being 10^{-9} mm Hg at 1500°K and 1.5×10^{-6} mm Hg at 2227°K. Between 1900°K and 2227°K, their data lie not too far from the line extrapolated from the average results^[8] obtained in this Laboratory for 10 mol-% UC-90 mol-% ZrC; but below 1900°K, their emission curve shows an abrupt change in shape. This is interpreted as being due to a change in the state of the surface. There is considerable scattering in their data, especially at temperatures below 1600°K; the data shown in Fig. 2 represent the upper limits of Anderson and Danforth's results at these temperatures. Haas^[7]

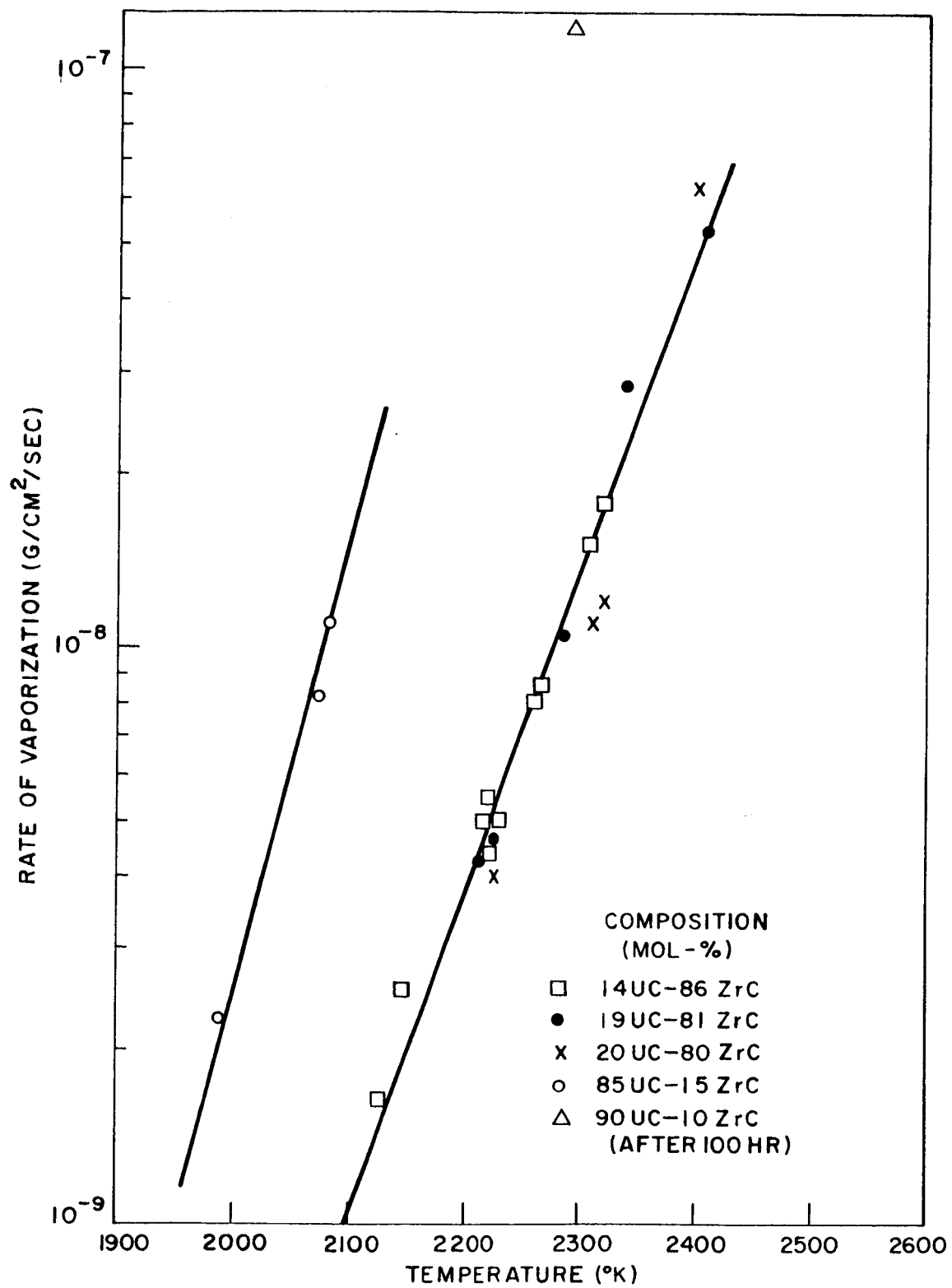


Fig. 1--Rate of vaporization of UC-ZrC system

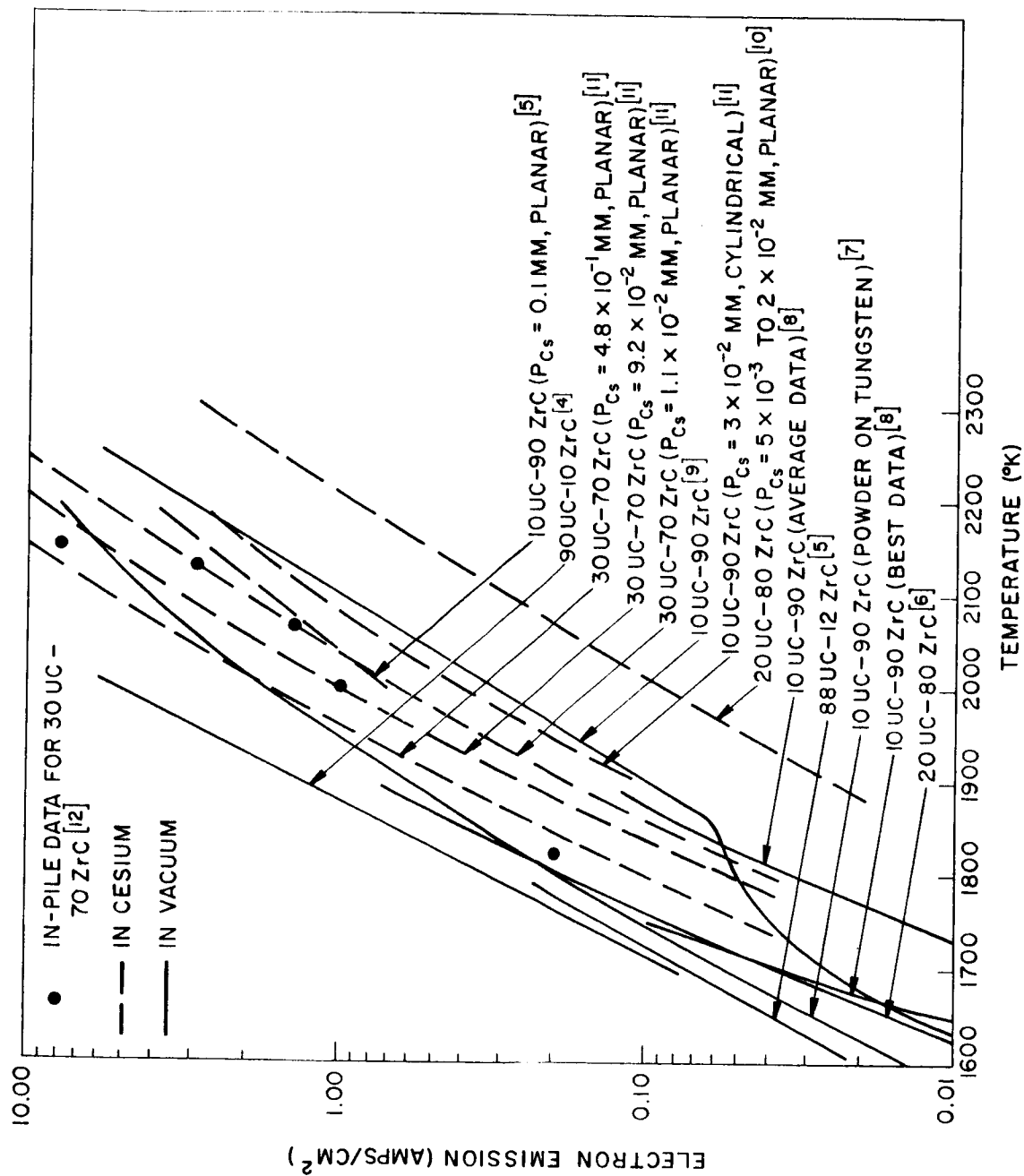


Fig. 2--Electron emission of UC-ZrC system (cylindrical and planar indicate shape of carbide cathode used)

has studied the emission of 10 mol-% UC-90 mol-% ZrC powder deposited on a tungsten filament up to 2200°K in 10^{-10} mm Hg vacuum. His data lie closer to our best 10 mol-% UC-90 mol-% ZrC data^[8] and the Los Alamos 20 mol-% UC-80 mol-% ZrC data^[6] than to the data of Anderson and Danforth.

If UC-ZrC is a dispenser cathode, as suggested by Haas^[7] and by Anderson and Danforth,^[9] then the rate of formation of the adsorbed uranium layer and the amount of surface coverage at the steady state should depend strongly upon the thermal history, the impurity contents, and the stoichiometry of the sample as well as on the ambient degree of vacuum. Perhaps for high-UC cathodes the uranium activity is high enough to maintain the adsorbed layer in spite of the existence of factors which tend to disrupt such a layer, whereas for low-UC cathodes the uranium activity is low and the adsorbed layer can easily be partially destroyed by any undesirable factor present. This, coupled with the possibility that high-ZrC samples may tend to dissolve more oxygen and nitrogen gaseous impurities, may explain why low-UC cathodes are more easily subject to poisoning. Further studies of the controlling factors of the emission of low-UC cathodes at temperatures of thermionic interest are definitely needed to clarify this confusing situation.

3. Although the short-circuit current density observed in a cesium cell depends upon the electrode spacing, the cesium pressure, and the nature of the operating mode, and has no significance with regard to evaluating the quality of a cathode material, it is interesting to note that the data obtained on 10 mol-% UC-90 mol-% ZrC cathodes in cesium lie close to the average vacuum emission data. In all cases, the short-circuit current densities increase as the cesium pressure increases. Furthermore, the short-circuit current densities obtained on electrically heated 30 mol-% UC-70 mol-% ZrC cathodes agree fairly well with the in-pile results.

Present Status of the Carbide Cathodes

The data shown in Figs. 1 and 2 can be used for the appraisal of the present status of the carbide cathodes with regard to their life expectancy and output performances. If an arbitrary figure of 5 amps/cm^2 is set as the minimum emission required, then for a 90 mol-% UC-10 mol-% ZrC cathode to provide such an emission, the material loss will be about 3 mils/yr. Under the same emission requirement, for low-UC cathodes (10 to 20 mol-% UC) the material loss will be about 2 mils/yr if the emission data of Haas^[7] are used, and about 7 mils/yr if the emission data of Anderson and Danforth^[9] are used.

It must be pointed out that the figures quoted above represent the worst possibilities, since they are deduced from vacuum emission data and vaporization rates in vacuum. In the presence of cesium, the output increases with the increase of cesium pressure and the vaporization rates probably decrease; the rates of material loss at an output of 5 amps/cm^2 are therefore less than these values. It must also be pointed out that the true evaluation of the cell performance should be based on the optimum power-density output rather than on short-circuit current densities. The optimum power-density output depends on the shape of the current versus voltage curve. Unfortunately, there are not enough data to enable comparisons to be made of the performances of cells using UC-ZrC cathodes of various compositions.

Metal-cathode System

The metal-cathode system operates in the temperature range from 1600° to 1900°K . The electron emissions of the refractory-metal emitters are determined by the adsorption characteristics of cesium on the emitter surfaces. The critical materials problem here is not the vaporization loss of emitter materials, but the interaction between the emitter and the nuclear fuel, which may impair the mechanical and electron-emission stability of

the emitter. The diffusion between refractory-metal emitters--such as tungsten, tantalum, molybdenum, niobium, and a number of uranium-containing fuels at high temperatures--have been studied at this Laboratory, and the results are being presented in a separate paper at this meeting.

It must be emphasized that even in cases where no significant diffusion occurs, so that the mechanical stability of the emitter is not impaired, the electron emission of the emitter may still be affected by the migration of the components of the fuel (such as uranium), either in solution state or, more likely, through the grain boundaries of the emitter, to the emitter surface to form an adsorbed layer there. This would change the work function of the emitter surface and thus its cesium-adsorption characteristics and emission performance. The earlier work by Langmuir on tungsten containing ThO_2 [13, 14] and by Dushman, Dennison, and Reynolds on tungsten containing UO_2 , ZrO_2 , and rare-earth oxides [15] all pointed to such a possibility. Their samples consisted of tungsten with a small amount (~1%) of the oxides dispersed in it.

To simulate the arrangement of a fueled metal-cathode system, we have carried out the following experiments. [16] A thin wafer (20 mils thick) of UO_2 was sandwiched between two molybdenum disks, the top one 20 mils thick and the bottom one 1/16 in. thick. The edges of the disks were electron-beam welded in vacuum, and the emission from the surface of the thin molybdenum disk was followed as a function of time in a vacuum of 10^{-8} mm Hg, using standard guard-ring anode geometry and electron-bombardment heating. The sample was held at 2300°K for 2 hr and then in the temperature range from 1675° to 1900°K for about 200 hr before the data shown in Fig. 3 were obtained. During this period, enough uranium diffused to the surface of the molybdenum disk so that the emission was much higher than that of pure molybdenum. It can be seen from the figure that after flashing at 2300°K for 5 min the adsorbed uranium was completely driven off, since after cooling down to 1675°K the emission corresponded

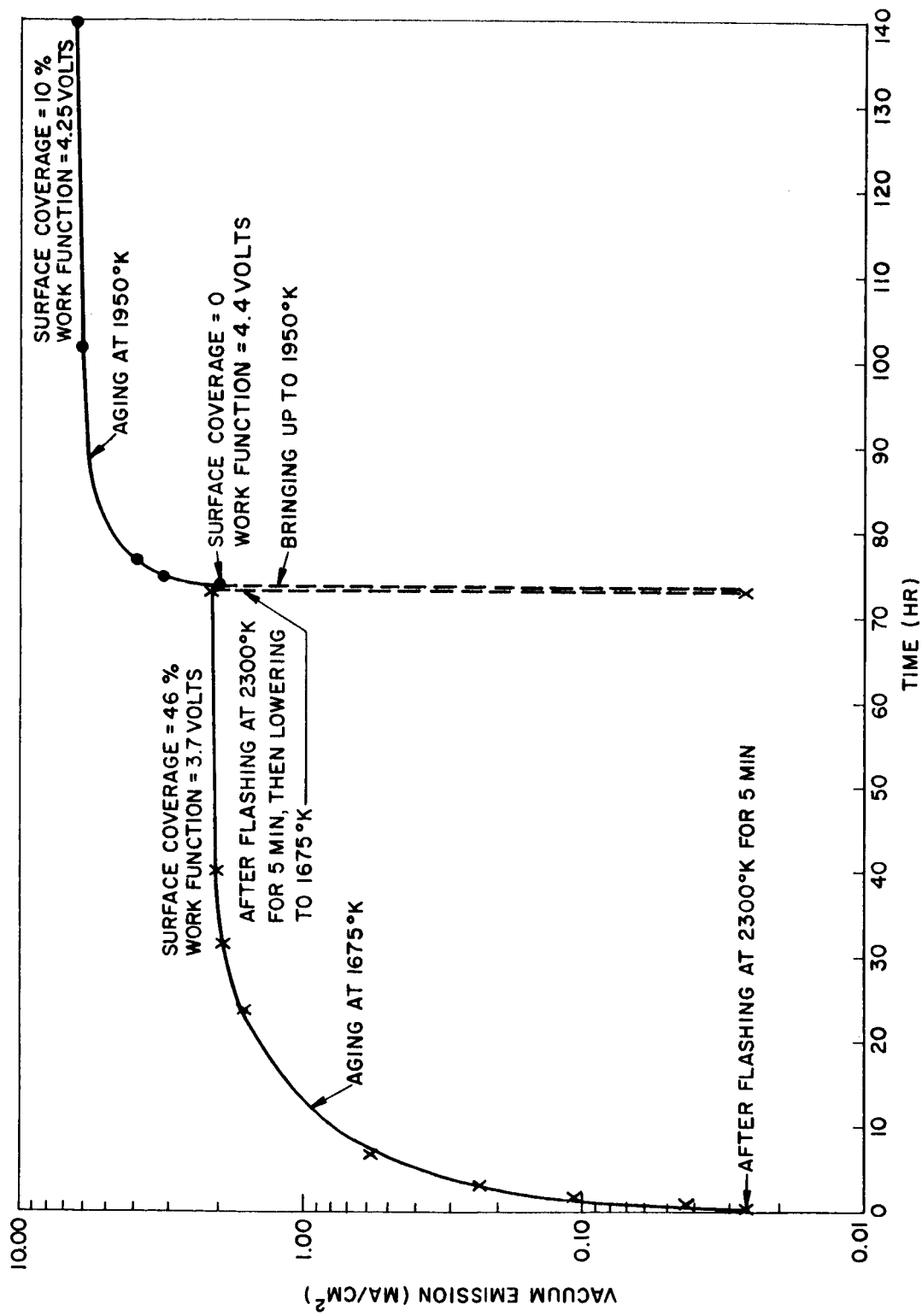


Fig. 3--Change in vacuum emission of molybdenum in contact with UO₂ with time at various temperatures; sample was heated to 2300°K for 2 hr and subsequently maintained in the temperature range from 1675° to 1900°K for 200 hr before these data were obtained

to that of pure molybdenum at this temperature. On aging at 1675°K , the emission increased gradually owing to the increase of surface uranium coverage caused by diffusion from the bulk. Finally, a steady state was reached where the amount of uranium reaching the surface by diffusion was just balanced by the amount of uranium lost from the surface by evaporation. The surface coverage, θ , at this steady state was about 46%, as calculated from the equation $\theta = (\log i - \log i_0)/(\log i_1 - \log i_0)$, where i is the emission at the steady state, i_0 is the emission of pure molybdenum at the same temperature, and i_1 is the emission of a fully covered surface at the same temperature (calculated by assuming a work function of 2.9 volts for such a surface).

Also shown in Fig. 3 is an activation curve at 1950°K , the steady-state surface coverage being about 10%. This implies that although the rate of diffusion is higher at 1950°K than at 1675°K , the much more rapid increase in vaporization rate with temperature outweighs this, with the result that the net accumulation of uranium on the surface is actually less at 1950°K than at 1675°K . Both the rate of activation and the steady-state surface coverage are probably functions of the thermal history and the microstructure (such as grain sizes and orientations) of the emitter material. However, it remains true that once the emitter is contaminated by components (such as uranium) of the fuel, it would be more advantageous to run it at a higher, rather than a lower, temperature in order to drive off the uranium arriving at the surface--assuming, of course, that such an adsorbed layer of uranium is detrimental to the performance of the cell. It must be pointed out that other fission products may behave similarly to UO_2 (as indicated by the work of Dushman, et al., on tungsten containing ZrO_2 , CeO_2 , and La_2O_3 [15]), especially if these fission products are formed at the grain boundaries in situ by the fission of the uranium atoms arriving there by diffusion. How serious the effect of such an adsorbed layer is on the performance of the emitter in the presence of cesium, and how the

thermal history of the cathode system affects the rate of activation and the amount of the surface coverage at the steady state are questions which must be answered before selection of the proper operating temperatures for the metal-cathode system can be made.

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